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High-pressure synthesis of MnO–ZnO solid solutions with rock salt structure: *in situ* X-ray diffraction studies

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X-ray diffraction with synchrotron radiation has been used for the first time to study chemical interaction in the MnO–ZnO system at 4.8 GPa and temperatures up to 1600 K. Above 750 K, the chemical reaction between MnO and ZnO has been observed that resulted in the formation of rock salt (rs) $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ solid solutions ($0.3 \leq x \leq 0.7$). The lattice parameters of these solid solutions have been *in situ* measured at high pressures as a function of temperature and corresponding thermal expansion coefficients have been calculated.

Keywords: zinc oxide; manganese (II) oxide; solid solutions; high pressure; high temperature

1. Introduction

Zinc oxide is a wide-band-gap semiconductor and has many industrial applications [1,2]. Recently, ZnO-based solid solutions with transition metal oxides have gained substantial interest as promising magnetic semiconductors [2]. At ambient pressure, ZnO has a hexagonal wurtzite structure ($P6_3mc$) that transforms into a rock salt structure ($Fm\bar{3}m$) at pressures above 6 GPa [3,4]. The high-pressure phase of ZnO is kinetically stable only above 2 GPa and cannot be quenched down to ambient conditions [4]. Very recently, metastable $\text{Me}^{\text{II}}\text{O}$ –ZnO solid solutions ($\text{Me}^{\text{II}}\text{–Ni}^{2+}$, Fe^{2+} , Co^{2+} , Mn^{2+}) with a rock salt structure have been synthesized by quenching from 7.7 GPa and 1450–1650 K [5]; in particular, single-phase rock salt (rs) $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ (MnZO) solid solutions of various stoichiometries ($0 < x \leq 0.4$) have been obtained. A thermodynamic study of the MnO–ZnO system has shown that at ambient pressure there is a wide (from 10 to 75 mol% ZnO at 1073 K) region of coexistence of rs-MnO-based and wurtzite ZnO-based solid solutions [6]. However, no information on chemical interaction and phase relations in the system at high pressures and temperatures can be found in the literature. In the present work, we have performed

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the first *in situ* study of the binary MnO–ZnO system at high pressures and temperatures using X-ray diffraction with synchrotron radiation.

2. Experimental

High-purity powders of wurtzite ZnO (Alfa Aesar, 99.99%, 325 mesh) and rs-MnO (Alfa Aesar, 99.99%, 325 mesh) have been used as starting materials. The MnO–ZnO mixtures of various compositions (0, 30, 50 and 70 mol% ZnO) were thoroughly ground in a mortar, compressed into disks and placed into capsules of high-purity hexagonal graphite-like boron nitride (hBN).

High-pressure experiments have been performed using a MAX80 multianvil X-ray system at Beamline F2.1, DORIS III (HASYLAB-DESY). The experimental details and high-pressure setup have been described elsewhere [7,8]. Energy-dispersive X-ray diffraction patterns were collected on a Canberra solid-state Ge detector with fixed Bragg angle $2\theta = 9.073(1)^\circ$ using a white beam collimated down to $100 \times 100 \mu\text{m}^2$. The detector was calibrated using the K_α and K_β fluorescence lines of Rb, Mo, Ag, Ba and Tb.

The sample temperature was measured by a Pt10%Rh–Pt thermocouple. The correction for the pressure effect on the thermocouple emf was made using the data of Getting and Kennedy [9] extrapolated to 5 GPa. The temperature in the high-pressure cell was controlled by a Eurotherm PID regulator within ± 3 K. Pressures at various temperatures were evaluated from the lattice parameters of highly ordered ($P_3 = 0.98 \pm 0.02$)¹ hBN using its thermoelastic equation of state [7]. With the temperature growth up to 1600 K, the pressure increase in the central part of the cell did not exceed 0.2 GPa.

The samples were compressed to the required pressure at ambient temperature, and then diffraction patterns were collected in the “autosequence” mode at a linear heating with a rate of 10 K/min. With the storage ring operating at 4.44 GeV and 120 ± 30 mA, the time of data collection for each pattern was 60 s.

3. Results and discussion

At 4.8 GPa and temperatures below 730 K, only reflections of pristine oxides (w-ZnO and rs-MnO) are observed in the diffraction patterns. Appearance of new reflections corresponding to the rs-Mn_{1-x}Zn_xO solid solutions has been observed at temperatures starting from ~ 735 K (Table 1). Regardless of the stoichiometry, the lattice parameters of the forming solid solution are very different from those of pristine rs-MnO (Table 2), contrary to the FeO–ZnO system [10]. Upon further temperature increase, intensities of w-ZnO and rs-MnO reflections start to decrease, indicating a chemical interaction in the system. This reaction is accompanied by the dissolution of zinc oxide in manganese (II) oxide and the formation of a Mn_{1-x}Zn_xO solid solution with

Table 1. Characteristic temperatures of chemical interaction in the MnO–ZnO system at 4.8 GPa.

Temperature	ZnO/(MnO + ZnO) molar ratio		
	0.3	0.5	0.7
T_s (K)	733	743	803
T_d (K)	943	1043	1243
T_{cd} (K)	1093	1243	1343

Note: T_s is the onset temperature of rs-MnZO formation, T_d the temperature of complete disappearance of w-ZnO and T_{cd} the temperature of complete disappearance of rs-MnO; in all cases the error is ± 5 K.

Table 2. Lattice parameters and volume thermal expansion coefficients of rock salt MnO–ZnO solid solutions at 4.8 GPa.

Composition	MnO	Mn _{0.7} Zn _{0.3} O	Mn _{0.5} Zn _{0.5} O	Mn _{0.3} Zn _{0.7} O	rs-ZnO ^a
Lattice parameters at 1298 K (Å)	4.450(4)	4.415(3)	4.376(4)	4.349(5)	4.305
$\alpha \times 10^5$ (K ⁻¹)	3.36 ± 0.37	6.96 ± 0.33	7.4 ± 0.45	7.69 ± 1	8.2 ± 0.9
Temperature range (K)	800–1500	943–1500	1043–1500	1243–1500	–

Note: ^aLinear extrapolation of the thermal expansion coefficients and lattice parameters of rs-Mn_{1-x}Zn_xO ($x = 0, 0.3, 0.5, 0.7$) solid solutions to $x = 1$ (rs-ZnO).

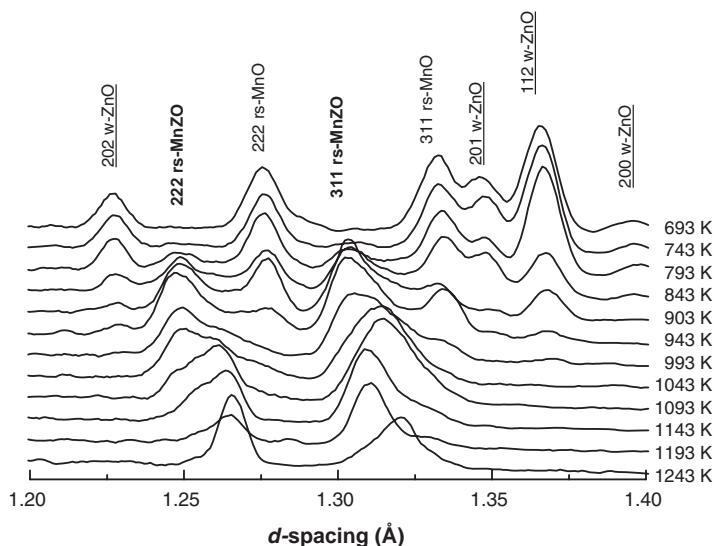


Figure 1. Diffraction patterns of the MnO–ZnO mixture (50 mol% ZnO) taken at 4.8 GPa in the course of linear heating at a rate of 10 K/min.

a rock salt structure. The forming MnZO solid solution coexists with w-ZnO and rs-MnO in a rather wide temperature range. The temperature of complete disappearance of w-ZnO (T_d) depends on the initial stoichiometry, as shown in Table 1, and increases with ZnO content from 943 ± 5 K for $x = 0.3$ to 1243 ± 5 K for $x = 0.7$. At higher temperatures ($>T_d$), only reflections of rs-Mn_{1-x}Zn_xO (as the main phase) and rs-MnO (as the impurity) are observed in the diffraction patterns. The temperature of complete disappearance of rs-MnO (T_{cd}) varies from 1100 to 1350 K depending of the stoichiometry (Table 1), and ultimately only reflections of rs-MnZO phase remain in the diffraction patterns (Figure 1). The compositions of the as-formed rs-MnZO solid solutions thus attain the compositions of the initial reaction mixtures.

Quenching down to ambient conditions results in the formation of single-phase rs-Mn_{1-x}Zn_xO solid solutions only at relatively low ZnO concentration, *i.e.* $x \leq 0.4$. The recovered samples with a higher ZnO content are two-phase mixtures of MnZO solid solutions with rock salt and wurtzite structures, which are in a good agreement with our previous results on the synthesis of MnO–ZnO solid solutions by quenching from 7.7 GPa [5].

Similar to the FeO–ZnO system [10], at temperatures above 1400 K drastic changes in the intensities of reflections are observed in diffraction patterns for all rs-MnZO solid solutions.² Such fluctuations of intensities can be caused by the inferred motion of crystallites due to the appearance of a liquid in the system that is typical for an onset of melting. It should be noted that at ambient pressure, the melting points of w-ZnO and rs-MnO are 2248 ± 25 K [11] and 2123 ± 20 K [12], respectively, but dp/dT slopes for their melting curves are not known. In the case of rs-Mn_{0.5}Zn_{0.5}O, at 4.7 ± 0.2 ГПа, we observed complete melting at 1643 ± 20 K.

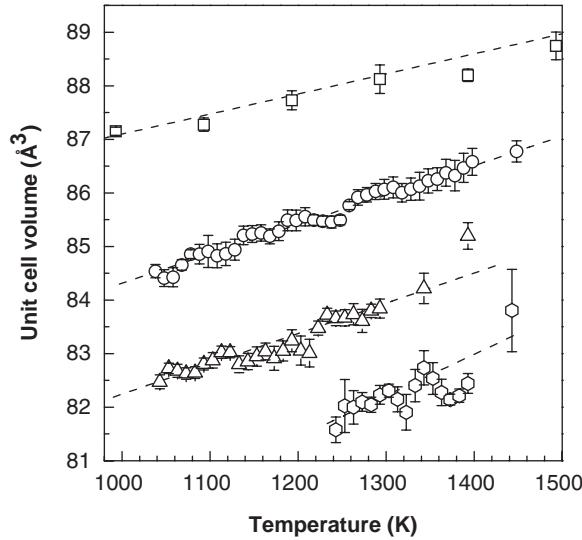


Figure 2. Unit cell volumes of rock salt $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ solid solutions vs. temperature at 4.8 GPa (squares – $x = 0$; circles – $x = 0.3$; triangles – $x = 0.5$; hexagons – $x = 0.7$).

Lattice parameters of rs- $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ solid solutions ($x = 0.3, 0.5, 0.7$) have been determined in the T_d –1500 K range at 4.8 GPa. The linear temperature dependencies of the unit cell volumes are shown in Figure 2, and their slopes give the values of the volume thermal expansion coefficients (α) at 4.8 GPa (Table 2). The thermal expansion coefficient for pure manganese (II) oxide, $3.3(4) \times 10^{-5} \text{ K}^{-1}$, is in good agreement with the value $3.45(1) \times 10^{-5} \text{ K}^{-1}$ reported in [13]. Linear extrapolation of the thermal expansion coefficients of rs- $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ solid solutions to $x = 1$ (rs-ZnO) gives the value of $8.2(9) \times 10^{-5} \text{ K}^{-1}$.

4. Conclusions

At pressures of about 5 GPa and temperatures above 750 K, chemical interaction between MnO and ZnO results in the formation of $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ ($0.3 \leq x \leq 0.7$) solid solutions with the rock salt structure. The temperature of the formation of single-phase rs- $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ increases with increasing ZnO content from 943 K for $x = 0.3$ to 1243 K for $x = 0.7$. Thermal expansion coefficients calculated from the temperature dependencies of lattice parameters of rs- $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ solid solutions under pressure are intermediate between the corresponding values of pristine MnO and ZnO.

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Notes

1. ($P_3 = 1 - \gamma$), where γ is the concentration of turbostratic stacking faults [14].
2. For rs- $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{O}$, an abrupt (by more than one order of magnitude) increase in the intensity of the 220 reflection is observed, while 331 and 400 reflections disappear almost completely; for $\text{Mn}_{0.3}\text{Zn}_{0.7}\text{O}$, 311 and 420 reflection

intensities increase twice, and the intensity of 220 and 511 reflections decreases. No changes in reflection intensities are observed for pristine manganese (II) oxide at the same p , T conditions.

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